ANGLO-CHINESE JUNIOR COLLEGE
DEPARTMENT OF CHEMISTRY
Preliminary Examination

CHEMISTRY H2
Paper 3 Free Response

9647/03
29 August 2012
2 hours

Candidates answer on separate paper.

Additional Materials: Data Booklet
Answer Paper
Cover Page

READ THESE INSTRUCTIONS FIRST

Write your index number, name, form class and tutorial class on all the work you hand in.
Write in dark blue or black pen.
You may use a pencil for any diagrams, graphs, or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluids.

Answer any **four** questions.
A Data Booklet is provided.
You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question of part question.
At the end of the examination, fasten all your work securely together.

This document consists of **12** printed pages and **1** blank page.

Answer any **four** questions.

1 (a) When hydrochloric acid is added to sodium thiosulfate, $Na_2S_2O_3$, a fine precipitate of sulfur appears. This gradually makes the solution opaque.

$$Na_2S_2O_3(aq) + 2\,HCl(aq) \longrightarrow S(s) + SO_2(g) + 2\,NaCl\,(aq) + H_2O(l)$$

The rate of the reaction may be determined by measuring how long it takes for the solution to become opaque such that a cross marked on a piece of paper placed under the beaker containing the reaction mixture just becomes obscured.

A series of experiments were carried out to study the order of reaction with respect to $Na_2S_2O_3$ and the following results were obtained.

Experiment Number	Volume / cm^3			Time / s
	HCl	$Na_2S_2O_3$	H_2O	
1	20.0	40.0	40.0	39
2	20.0	30.0	50.0	50
3	20.0	20.0	60.0	83
4	20.0	10.0	70.0	170

(i) Explain why the total volume of the reaction mixture is kept constant for all the four experiments.

(ii) Calculate the values of $(\frac{1}{\text{Time}})/s^{-1}$ for the various volumes of $Na_2S_2O_3$ used.

(iii) Hence or otherwise, state how the rate changes with the volume of $Na_2S_2O_3$ used.

(iv) Explain why the rate changes with the volume of $Na_2S_2O_3$ used. **[5]**

(b) Sulfur reacts with chlorine gas to form a compound **A** containing 47.4% sulfur by mass. When compound **A** is reacted with water, a yellow precipitate was formed together with a solution containing a mixture of sulfurous acid, H_2SO_3 and hydrochloric acid, HCl.

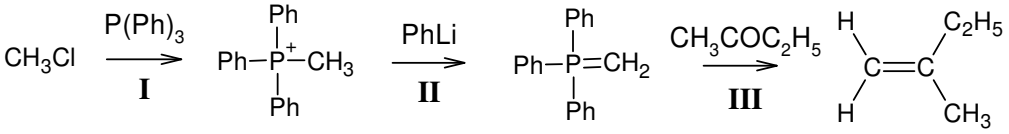
(i) Given that the relative molecular mass of **A** is 135, determine the empirical formula and the molecular formula of **A**.

(ii) Explain why compound **A** can react with water.

(iii) If 1.00 g of compound **A** was dissolved in water, calculate the volume of 1.00 mol dm^{-3} NaOH that would be required to completely neutralise the resultant solution. **[5]**

(c) The Wittig reaction was discovered by German chemist Georg Wittig. This reaction is significant because it uses a phosphorous-containing compound to produce an alkene molecule. In 1979, Georg Wittg was awarded the Nobel Prize for his work in discovering the Wittig reaction.

The Wittig reaction is thought to proceed through the following stages.



where Ph refers to phenyl substituent.

(i) What type of reaction takes place in stage **I**?

(ii) Describe the mechanism for stage **I**. In your answer, show any relevant charges, lone pair of electrons and movement of electrons.

(iii) State the role of PhLi in stage **II**.

(iv) Suggest the other product of stage **III** and hence construct the balanced equation for this stage.

(v) When butane reacts with chlorine under ultraviolet light, a mixture of monochlorobutane is produced. $P(Ph)_3$, PhLi and ethanal are then added in succession to the resultant mixture. This results in the formation of **two pairs** of geometric isomeric alkenes.

Suggest the structures of the four alkenes, and the ratio in which they might be produced. Explain your suggested ratio.

[10]
[Total: 20 marks]

2 (a) Silver chloride is a white crystalline solid well known for its low solubility in water. It is often used in photography as it darkens quickly when it is exposed to light.

(i) Explain what is meant by the *lattice energy of silver chloride*. Write an equation to represent the lattice energy of silver chloride.

(ii) Using the following data, and relevant data from the Data Booklet, construct a thermochemical cycle to calculate the lattice energy of silver chloride. Include state symbols in your cycle.

	Value / kJ mol^{-1}
Standard enthalpy change of formation of AgCl	-127
Standard enthalpy change of atomization of Ag	+285
First ionization energy of Ag	+731
First electron affinity of Cl	-349

(iii) Explain how you would expect the numerical magnitude of the lattice energy of silver chloride to compare with the lattice energy of silver iodide.

[7]

(b) Equal volumes of 0.020 mol dm^{-3} of aqueous silver nitrate and an **unknown** concentration of aqueous sodium chloride were mixed in a beaker. A white precipitate was observed. The precipitate formed was filtered and washed. A colourless solution was seen upon addition of aqueous ammonia to the white precipitate.

Solubility product, K_{sp}, of silver chloride is 1.77×10^{-10} mol^2 dm^{-6}.

(i) Write an expression for the solubility product of silver chloride.

(ii) Calculate the maximum concentration of aqueous sodium chloride such that no precipitate of silver chloride is formed upon mixing the two solutions.

(iii) Explain why a colourless solution is obtained when aqueous ammonia is added to the white precipitate.

[4]

(c) Iodine, a member of Group VII element, reacts with alkali at room temperature to form iodide and iodate(V) ions. Group II metals form iodate(V) compounds which can undergo decomposition to give metal oxide, iodine vapour and oxygen gas.

(i) Name the reaction between iodine and alkali and write balanced ionic equation for the reaction.

A student conducted an experiment to find out the thermal stability of $Ca(IO_3)_2$, $Sr(IO_3)_2$ and $Ba(IO_3)_2$. He took 2.0 g of each compound and heated them separately in a test-tube at a temperature **T** ºC. He recorded the time of the appearance of purple iodine vapour.

(ii) Briefly explain the relationship between thermal stability of iodate compounds with the time of appearance of purple iodine vapour.

(iii) Arrange $Ca(IO_3)_2$, $Sr(IO_3)_2$ and $Ba(IO_3)_2$ in the order of increasing thermal stability. Explain the trend as fully as you can.

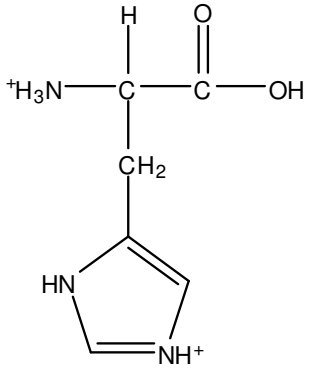
(iv) Solid sodium iodide undergoes reaction with concentrated sulfuric acid State the observations and write balanced equations for the reactions that take place.

[9]

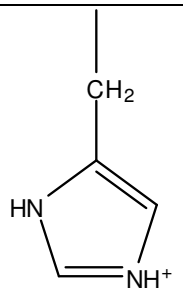
[Total: 20 marks]

3 (a) Histidine is an essential α-amino acid in humans and other mammals. Histidine is utilized by the body to develop and maintain healthy tissues. It is especially important in the myelin sheath that coat nervous cells to ensure the transmission of messages from the brain to organs throughout the body. Therefore, adequate histidine levels are essential to good mental and physical health. Food such as yellowfin tuna, mackerel and cauliflowers are excellent sources of histidine.

The structure of the fully protonated form of histidine is given below.



The pK_a values of the respective functional groups are provided in the following table.

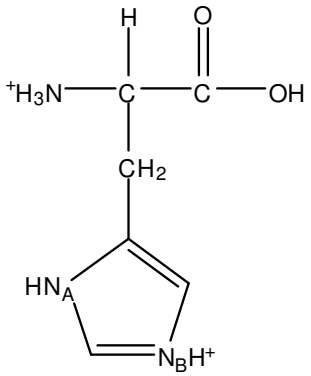
Functional group	pK_a value
-COOH	1.82
$-NH_3^+$	9.17
	6.00

(i) Make use of the pK_a values to suggest the major species present in solutions of histidine with the following pH values.

- pH 1
- pH 4
- pH 8
- pH12

(ii) Explain, with the aid of relevant chemical equation(s), how histidine acts as a buffer at pH of 1.82.

(iii)



As shown in the structure of the fully protonated histidine above, the side chain of the fully protonated histidine has 2 different N atoms, N_A and N_B atom. N_B atom is protonated but not N_A atom. The heterocyclic ring of the side chain is known to be as stable as benzene ring.

Explain why N_A atom cannot be protonated. **[7]**

(b) Histidine is also important for our digestion as it helps to produce gastric juices in the stomach. However, high level of histidine causes acid indigestion which is also known as heartburn. Heartburn results in burning sensation at the upper stomach as the stomach acid rises into the esophagus. The pH of the stomach of a patient who suffers from heartburn is 4.

A stomach juice sample is extracted from a patient to determine the concentration of histidine using sodium hydroxide, NaOH (aq).

(i) Draw a labeled titration curve of pH against amount of NaOH (aq) added when 1 mole of fully protonated histidine is titrated with NaOH.

You should clearly label the following in your titration curve.

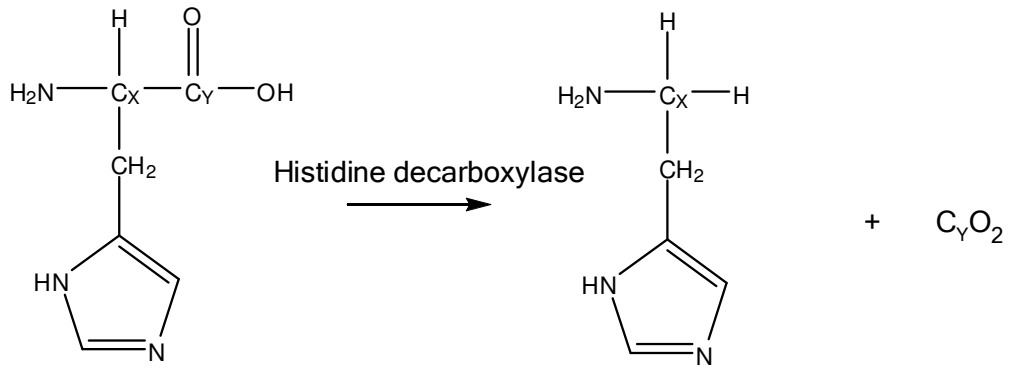
- Equivalence point(s).
- Maximum buffer capacities.

(ii) Write a balanced equation of the reaction between histidine in the patient's stomach juice sample and NaOH.

[5]

(c) Histidine is converted to histamine by an enzyme known as histidine decarboxylase. Histamine increases the permeability of the capillaries to white blood cells, to allow them to engage harmful pathogens in infected body tissues.

Histidine decarboxylase has a quaternary protein structure. The enzyme-catalysed decarboxylation reaction is shown below.



Histidine Histamine

The decarboxylation of histidine occurs in the active site of histidine decarboxylase. In one part of the enzyme's active site, there is a section of 11 amino acid residues which is critical in the catalysis of decarboxylation of histidine.

In addition, the active site also causes some of the bond angles in histidine molecule to deviate from its ideal bond angles. Consequently, the catalysis of decarboxylation of histidine is further increased.

(i) Explain what is meant by the term *quaternary structure of protein.*

(ii) Histidine decarboxylase undergoes enzymatic partial hydrolysis. Upon hydrolysis, the polypeptide fragments of the critical section of the enzyme's active site are isolated as shown below.

- Ala-Cys-Phe
- Gly-Gly
- Lys-Asp-Asp-Gly-Gly
- Phe-Arg-Lys
- Ala-Cys-Phe-Phe-Arg-Lys
- Asp-Asp-Gly

Deduce the sequence of the critical section of 11 amino acid residues of the enzyme's active site. Show your working clearly.

(iii) The C_X-C_Y bond in histidine is weakened during the enzyme-catalysed decarboxylation reaction.

Explain why the C_X-C_Y bond in histidine is weakened.

(iv) The decarboxylation reaction of histidine can be disrupted due to fever and lead poisoning.

Explain how the following conditions disrupt the decarboxylation reaction of histidine.

- Fever
- Lead Poisoning

[8]

[Total: 20 marks]

4 (a) Statistics show a correlation between road accidents and drivers who drink too much. One of the first chemical breathalysers was based on the oxidation process of ethanol using acidified potassium dichromate(VI).

(i) Derive the half equation for the oxidation of ethanol to ethanoic acid.

(ii) Hence, using relevant information from the Data Booklet, write a balanced ionic equation for the oxidation of ethanol using acidified potassium dichromate(VI).

The breathalyser kit consists of an inflated 1000 cm^3 plastic bag connected to a glass tube containing the dichromate crystals. When the breath is expelled through the tube the crystals change colour as they are reduced. The proportion of the crystals that change colour indicates the amount of alcohol present.

The current legal maximum blood alcohol concentration when driving is 80 mg per 100 cm^3 of blood. Alcohol concentration in the blood can be estimated by analysing the alcohol in the breath because an equilibrium is set up between the alcohol in the blood and the alcohol in the breath:

$CH_3CH_2OH(blood) \rightleftharpoons CH_3CH_2OH(breath)$

At body temperature, the concentration of alcohol in the blood is about 2300 times that in the breath.

(iii) What is the corresponding breath alcohol concentration in mg per 1000 cm^3 of breath?

(iv) What colour change would you expect for a positive result?

[4]

(b) Modern breathalysers use fuel-cell technology. The fuel cell has two platinum electrodes with a porous acid-electrolyte material sandwiched between them. As the exhaled air from the suspect flows past one side of the fuel cell, the platinum anode oxidizes any alcohol in the air to produce ethanoic acid.

The electrons produced flow through a wire from the platinum anode to the cathode. The protons move through the lower portion of the fuel cell to the cathode and combine with oxygen to form water. It is the size of this electric current which determines the amount of alcohol in the blood stream.

(i) Construct an equation for the cathode reaction.

(ii) Hence write a balanced equation for the overall reaction.

(iii) $\Delta G^{\ominus}$ and $E_{cell}^{\ominus}$ are related by the following equation, $\Delta G^{\ominus} = -nFE_{cell}^{\ominus}$

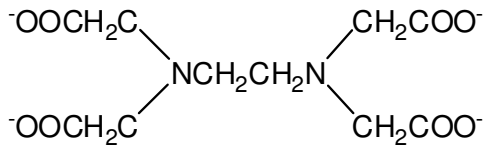
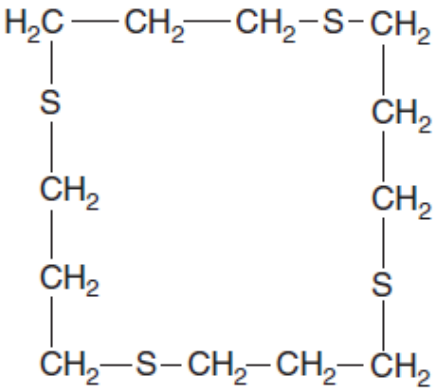
where $\Delta G^{\ominus}$ is the standard free energy change in J mol^{-1}, n is the number of electrons transferred during the redox reaction and F is the Faraday constant.

$\Delta G^{\ominus}$, for the oxidation of ethanol to ethanoic acid at 298 K, is -374 kJ mol^{-1}.

Use the equation you have written in **(b)(ii)** to decide on a suitable value for n and hence calculate the $E_{cell}^{\ominus}$ for the fuel cell breathalyser.

[4]

(c) EDTA (compound **B**) and the 'crown thioether' (compound **C**) are polydentate ligands that are used to remove harmful metals from the environment.

 **B**	 **C**
Compound **B** complexes with Cu^{2+} and can be used to remove Cu^{2+} from contaminated water.	Compound **C** complexes with Ni^{2+} and can be used to extract Ni^{2+} from solutions of industrial waste.

(i) Explain what is meant by a ***polydentate*** ligand and state the features present in both compounds **B** and **C** which make them suitable to act as ligands.

(ii) For both complexes formed between compound **B** and Cu^{2+} ions and between compound **C** and Ni^{2+} ions respectively, suggest the co-ordination numbers and shapes of both complexes.

[4]

(d) When water ligands in a hydrated metal ion are substituted by other ligands, the equilibrium constant for the reaction is referred to as the stability constant, K_{stab}, of the new complex.
For example,

$$[Ni(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq) + 6H_2O(l)$$

$$K_c = K_{stab} = \frac{[Ni(NH_3)_6]^{2+}}{[Ni(H_2O)_6]^{2+}[NH_3]^6}$$

The table below lists the colours and stability constants (in logarithm form) of some nickel(II) complexes.

Complex		lg K_{stab}	Colour
D	$[Ni(H_2O)_6]^{2+}(aq)$	-	green
E	$[Ni(NH_3)_6]^{2+}(aq)$	7.7	blue
F	$[Ni(H_2NCH_2CH_2NH_2)_3]^{2+}(aq)$	18.3	purple
G	$[Ni(EDTA)]^{2-}(aq)$	19.0	blue
H	$[Ni(CN)_4]^{2-}(aq)$	31.1	Pale yellow

(i) The standard free energy change, $\Delta G^{\ominus}$, and the stability constant, K_{stab}, are also related by the following equation,

$\Delta G^{\ominus} = -2.3RT \lg K_{stab}$ …….**(1)**

where R is the molar gas constant, T is the temperature in Kelvin and K_{stab} is the stability constant.

Using this equation [$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$] and the above equation **(1)**, explain why $[Ni(H_2NCH_2CH_2NH_2)_3]^{2+}$ has a higher lg K_{stab} than that of $[Ni(NH_3)_6]^{2+}$ even though both complexes have six Ni^{2+}-N dative bonds.

[You may represent $[Ni(H_2NCH_2CH_2NH_2)_3]^{2+}$ as $[Ni(en)_3]^{2+}$]

(ii) Use the data in the table to predict and explain what you will observe when a solution of pale yellow $[Ni(CN)_4]^{2-}$ is treated with EDTA.

(iii) The following table lists the colours of the photons of light of certain wavelengths.

Colour of photon	violet	blue	green	yellow	red
Wavelength/nm	400	450	500	600	650

Based on the observed colours of the complexes, deduce which complex, **D** or **H**, will have a larger energy gap between the two groups of 3d orbitals? Explain your answer.
Predict the colour of $[Ni(H_2O)_4(H_2NCH_2CH_2NH_2)]^{2+}(aq)$.

[8]

[Total: 20 marks]

5 **(a)** The molecules of ethanoic acid and methyl methanoate contain the same number of electrons. These molecules have the same mass and size but their boiling points differ widely.

Compound	Boiling point /°C
CH_3COOH	112
$HCOOCH_3$	32

(i) Suggest an explanation for the difference in boiling point.

(ii) Draw a diagram showing why ethanoic acid can dimerise in methyl methanoate.

[3]

(b) The classic synthesis of an ester is done via the Fischer Esterification, which involves treating a carboxylic acid with an alcohol in the presence of a catalyst.

The reaction between butanoic acid and ethanol produces ethyl butanoate, an ester which smells like pineapples.

$$CH_3CH_2CH_2COOH + CH_3CH_2OH \overset{H^+}{\rightleftharpoons} CH_3CH_2CH_2COOCH_2CH_3 + H_2O$$

An alternative way of producing ethyl butanoate is to mix ethanol with the acid chloride, butanoyl chloride.

(i) State the name of the reaction between butanoyl chloride and ethanol.

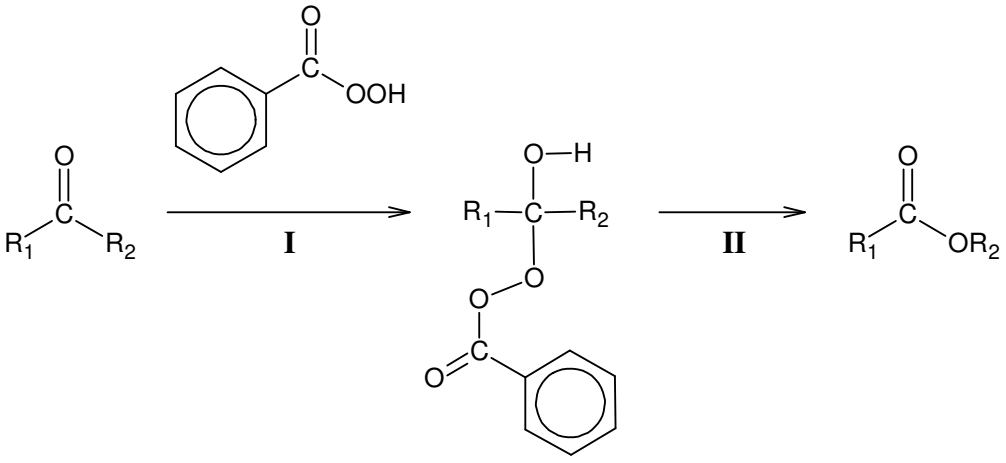
(ii) Using relevant data from the Data Booklet, explain why the acid chlorides are more reactive than the carboxylic acid in the reaction to form esters.

(iii) Suggest and explain **one** safety precaution you should employ when using acid chlorides in the laboratory.

[5]

(c) In 1899 the German chemists Adolf von Baeyer and Victor Viliger discovered that by treating ketones with peroxyacids, such as peroxybenzoic acid (C_6H_5COOOH), gives an ester by "insertion" of one atom of oxygen.

The Baeyer-Viliger reaction is thought to proceed through the following stages.



For asymmetrical ketones the oxygen atom is inserted in the order: tertiary alkyl > secondary alkyl > primary alkyl > CH_3.

(i) Peroxybenzoic acid can be formed by reacting benzoic acid and hydrogen peroxide. Write the balanced equation of this reaction.

(ii) State the role of peroxybenzoic acid in the Baeyer-Viliger reaction.

(iii) What type of reaction takes place in stage **I**?

(iv) Suggest the other product of stage **II**.

(v) Molecules of compound **J**, $C_6H_{12}O$ are chiral. The bond angles about all the carbon atoms are approximately 109.5°. When H_2O is eliminated from **J**, a mixture of three isomeric alkenes, C_6H_{10}, is produced. Only two of which are optical isomers of each other. Heating compound **J** with acidified potassium permanganate produces **K**, $C_6H_{10}O$. Mixing compound **K** with peroxybenzoic acid produces **one** compound **L** as the product.

Suggest the structures of **J**, **K, L** and the three alkenes.

[9]

(d) Using your answers in **(c)(v)**, suggest a simple chemical test by which one of the alkenes and compound **J** could be distinguished from each other. Write any appropriate equation.

[3]

[Total: 20 marks]

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